SO_2 AND NOx REMOVAL AT AMBIENT TEMPERATURES USING ACTIVATED CARBON FIBERS

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Abstract
The activity of polyacrilonitrile (PAN) and pitch based activated carbon fibers (ACF) has been studied for the removal of SO_2 and the reduction of NOx from air at ambient temperatures. The PAN-ACF was found to be active for oxidizing SO_2 and hydrating the product of H_2SO_4. The acid flows down from the ACF bed, maintaining the activity for SO_2 removal, and allowing the acid to be recovered. The influences of temperature, humidity, and contact time on the rate of SO_2 removal will be presented.
The pitch-ACF , when further activated with H_2SO_4 at 400°C, was found to remove NOx at low concentrations (around 10ppm) by reaction with NH_3 at temperatures around 10°C and at 100% humidity. Hearing the air to reduce the relative humidity was found to effectively enhance activity. Further, heat treatment of the fibers in inert atmosphere before activation enhanced the activity under high humidity. The cause of catalytic activity in the ACFs will discussed.

Introduction

In spite of extensive efforts to keep the atmosphere clean, acid rain problem is still growing globally. Extensive and efficient removal of SOx and NOx from the atmosphere as well as flue gas is strongly wanted to be developed.
The present authors have been involved in the dry removal of SOx and reduction of NOx with NH_3 using activated carbon fibers (ACF). SOx in the flue gas was oxidatively adsorbed as H_2SO_4 on ACF at 100-150°C until its saturation, and was reductively recovered in concentrated SO_2, consuming C of ACF as CO_2 to regenerate the adsorption ability of ACF. Such a deSOx has been commercialized with cheaper active coke, and polyacrilonitrile based ACF (PAN-ACF) exhibited very high capacity to reduce the volume of the reactor. However, the adsorption-recovery/regeneration sequence consumption of not cheap C, and large volume of reactor may prohibit current application.
NOx in flue gas has been found to be reduced with NH_3 on active coke at 120°C. Hence the deSOx and deNOx has been performed on the same coke in the three moving bed sequence of deSOx, recovery/regeneration and deNOx. However, the catalytic activity is not satisfactory especially at ambient temperatures. ACFs were found very active for this reaction.
In the present study, removal of SO_2 to be recovered in H_2SO_4 and reduction of NOx in low concentration ($\approx$10ppm) were both examined at ambient temperatures (0-80°C) using PAN-ACF and pitch based ACF (pitch-ACF), respectively. Very simple cleaning of atmosphere can be performed by very handy ways.

Experimental

SO_2 removal

The SO_2 removal was carried out in the fixed bed flow reactor at 100, 80, 50, and 30°C using PAN-ACF as the catalyst. Its analysis is summarized in Table 1. The reactant gas contained 1000ppm SO_2, 5% O_2, 10, 20, and 30% H_2O and the balance N_2. The weight of ACF and total flow rate were 0.5 g and 100 ml, respectively. The SO_2 concentration in inlet and outlet gases were analyzed by a flame photometric detector.

NOx reduction

A pitch based active carbon fiber (OG-5A) was supplied from Osaka Gas in a yarn form. OG-5A was further activated with 12N-H_2SO_4(300 wt%) through impregnation, drying, and heat-

treatment up to 400°C for 4 h (abbreviated as OG-5A 3/400/4). The ACF was further activated with H_2SO_4 under the same conditions. The analysis and surface areas of the as-received and further activated ACF are also summarized in Table 1.
Reduction of NO with NH_3 was performed in a fixed bed U-shaped flow type reactor. The weight and length of fiber bed, flow rate, the concentraions of NO and NH_3 in air, and reaction temperatures were 0.5 g, 70 mm, 50 $ml \cdot min^{-1}$, 10-400 ppm, 10-400 ppm, and 0-30°C, respectively. Air was humidified at the reaction temperature or some temperatures lower by 5 to 25°C than the reaction temperature. Reactant and product gases were analyzed by NOx meter (ECL-77A, YANAGIMOTO Co.,Ltd.).

Results

Capture of SO_2 in recoverable H_2SO_4

Figure 1 illustrates the capture profile of SO_2 in an atmosphere of 5% O_2, 10% H_2O on PAN-ACF at a temperature range of 30-100°C. W/F of this series of runs in the figure was $5x10^{-3} g \cdot min \cdot ml^{-1}$ (SV≈3000h). At 100°C, SO_2 was completely removed for 5h on the ACF and then broke through completely after 11h. Under the conditions, the desulfurization process is obligated to consist of capture, and recovery/regeneration steps. A lower temperature of 80°C prolonged the period of complete removal of SO_2 until 9h when SO_2 in the outlet gas started to increase gradually to reach 65% of the inlet concentration at 27h and stayed at this concentration until at least 45h.
Aq. H_2SO_4 was found to fall down from the vertical reactor to be stored in the reservoir placed below the reactor. A further lower temperature of 50°C further prolonged the period of complete removal to 11h, delayed the increase of SO_2 concentration and reduced the stationary concentration after 45h to 35%. An ambient temperature of 30°C allowed complete removal up to at least 60h. The SO_2 concentration while its complete removal was as low as 10 ppm at highest.
Figure 2 illustrates the influences of humidity on the removal of SO_2 at 100°C and 80°C. Higher humidity favored the deSOx by prolonging the period of complete removal and enhanced the stationary removal. Humidity of 20% allowed 20% stationary removal at 100°C. Lower temperatures emphasized the influences. Humidity of 20 and 30% provided 40 and 90 % stationary removal of SO_2 at 80°C respectively. At 50°C, complete removal could continue by humidity of 20% until at least 60h.
Figure 3 illustrates SO_2 removal at various W/F at 30°C. W/F of $5.0x10^{-3} g \cdot min \cdot ml^{-1}$ allowed complete removal of SO_2 when humidity was fixed at 10%. A half value of W/F reduced the removal to 90%, indicating catalytic process of SO_2 oxidation and hydration on the ACF.

Reduction of NOx on a pitch ACF and its activated ones

Figure 4 illustrates NO conversion at 22°C over a pitch (OG-5A) and its activated ones with H_2SO_4. The as-received ACF (Figure 4-1) provided a NO conversion of 50% at the start of the reaction, however the conversion decreased very rapidly to zero before 5h after the reaction started. Adsorption of NO is suspected. Activation of the ACF with H_2SO_4 increased the conversion very significantly (OG-5A-S(3/400/4) Figure 4-2) the stationary conversion after the rapid decrease with in 5h was as high as 60%.
Humidity in the feed gas retarded the reaction very significantly, as shown in Figure 4-3. The stationary conversion on OG-5A-S(3/400/4) in 100% humidity decreased 15%, which was, however, nontrivial.
Figure 5 illustrates influences of humidity on NO reduction at 22°C. Pitch ACFs all activated with sulfuric acid lost severally the activity by increasing humidity. It is noted that an ACF of higher surface area appeared to provide lower catalytic activity.

Heattreatment of ACFs

Influences of heattreatment to control the surface oxygen functional groups on ACF were examined on the NOx reduction. As shown in Figure 4, the heattreatment at 800°C (H-800) is very significant to provide an excellent conversion of 40% in dry air and 25% in wet air. Activation with H_2SO_4 (S(3/400/4)) of the heattreated ACF was also significant to provide conversions of 70% in dry air and 40% in wet air. The heattreatment at this temperature to the H_2SO_4 activated

ACF was interesting. The conversion in dry air decreased to 50% from 60%, but the conversion in wet air increased to 35% from 12%. Small retardation by humidity on the heattreated ACF is also shown in Figure 5.

Discussion

SO_2 removal

The present study succeeded to capture SO_2 and recover it in H_2SO_4. The PAN-ACF showed excellent activity to oxidize and hydrate SO_2 and to push H_2SO_4 flow down through its bed. PAN-ACF is very unique to show such a high oxidation activity very probably through its oxygen and nitrogen surface functional groups. Their cooperation may increase the oxidation activity. Humidity appeared very essential for the present process. Hydration of SO_3 and some dilution of H_2SO_4 may be keys to allow H_2SO_4 to flow down. Surface functional groups on ACF should interact with H_2O vapor. Hence their control may allow the smaller humidity for the recovery of H_2SO_4.

NOx

The ACF surface can activated NOx and NH_3 at the same time to reduce the former into N_2 as discussed in previous papers. The major concept in the present study is related in the retardation of water vapor which certainly inhibits on adsorption of NO. At temperature above 100°C, such a retardation is rather negligible but becomes distinct at room temperature probably because of the high coverage by condensation. Hence hydrophobic pitch ACF is effective. Its heattreatment may delicately control the surface functional groups to enhance the catalytic activity. In previous papers, the authors emphasized the importance of NH_3 adsorption in the NO-NH_3 reaction since adsorption of NH_3 is slightly disturbed with water vapor. However, the heattreatment enhances the activity in spite of a significant decrease of NH_3 adsorption. Activation of NO should be emphasized, although active sites for NO is not clarified yet.

In conclusion, PAN-ACF and pitch ACF are found very useful to capture SO_2 and reduce NO at ambient temperatures. Their practical application appears feasible.

Table 1 Profiles of ACFs

	Elemental Analysis(%)						Surface area
	C	H	N	O	S	Ash	(m^2/g)
FE-300	78.1	1.4	4.5	16.0	-	0.3	1141
OG-5A	92.3	1.0	0.8	5.6	tr.	0.3	680
OG-5A(3/400/4)	80.0	1.5	0.7	16.1	0.7	1.0	770

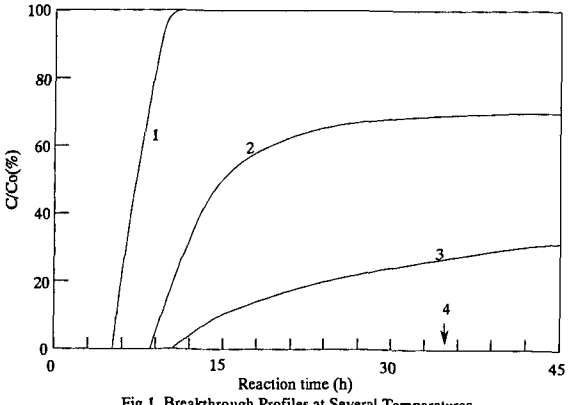

Fig.1 Breakthrough Profiles at Several Temperatures
SO_2 1000ppm, O_2 5%, W/F=5.0x10^{-3} g · min · ml^{-1}

1 : 100℃
2 : 80℃
3 : 50℃
4 : 30℃

No.4 adsorbed SO_2 completely at least 60 hours

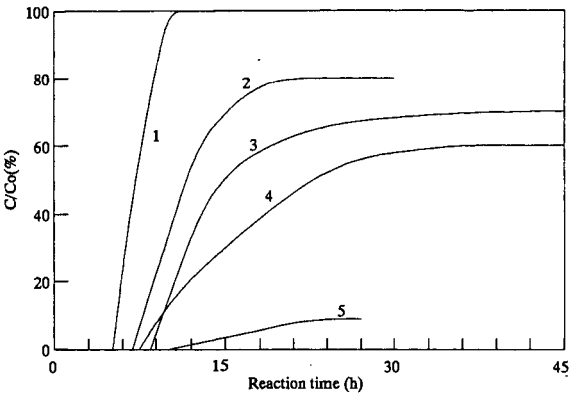

Figure.2 Influence of H_2O Concentration for SO_2 Removal
SO_2 1000ppm, O_2 5%, W/F=5.0×10^{-3}g · min · ml^{-1}

1 : 100℃, H_2O 10%
2 : 100℃, H_2O 20%
3 : 80℃, H_2O 10%
4 : 80℃, H_2O 20%
5 : 80℃, H_2O 30%

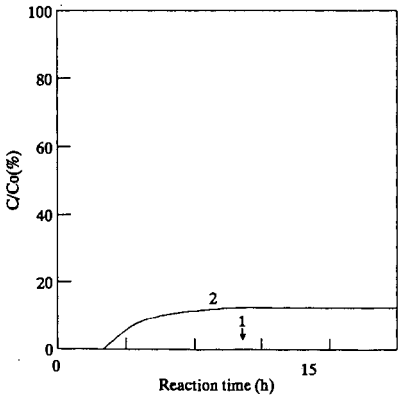

Fig.3 Effect of W/F for SO_2 Removal at 30℃
SO_2 1000ppm, O_2 5%, H_2O 10%

1 W/F=5.0×10^{-3}g · min · ml^{-1}
2 W/F=2.5×10^{-3}g · min · ml^{-1}

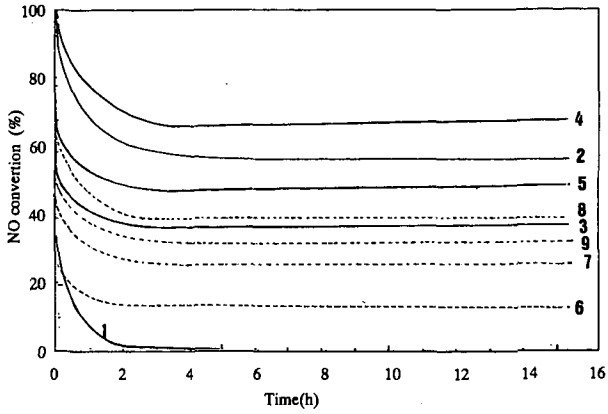

Figure 4 Conversion of NO in dry and wet air at room temperature over ACFs further activated with H_2SO_4

NO 10ppm, NH_3 20ppm, W/F = 5×10^{-3} g · min · ml^{-1}
Temp. : 22℃

Dry air (r.h.:0%)	Wet air (r.h.:100%)
1 : OG-5A	
2 : OG-5A-(300/400/4)	6 : OG-5A-(300/400/4)
3 : OG-5A-H800	7 : OG-5A-H800
4 : OG-5A-H800-S(300/400/4)	8 : OG-5A-H800-S(300/400/4)
5 : OG-5A-S(300/400/4)-H800	9 : OG-5A-S(300/400/4)-H800

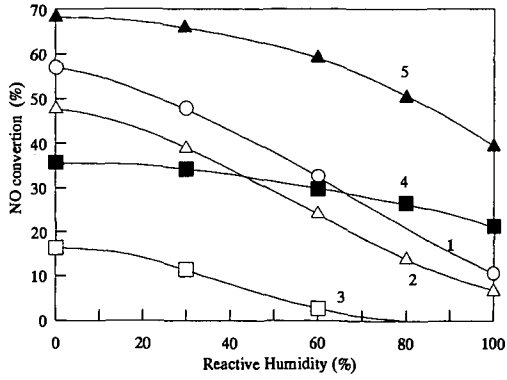

Figure 5 Stationary NO conversion vs. relative humidity(r.h)

Stationary conversion was observed at 15h after the reaction
NO 10ppm, NH_3 20ppm, W/F = 5×10^{-3} g · min · ml^{-1}
Temp. : 22℃

1 : OG-5A(3/400/4)	4 : OG-5A-H800
2 : OG-10A(3/400/4)	5 : OG-5A-H800-S(3/400/4)
3 : OG-20A(3/400/4)	